NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

Department of Chemical Engineering

B.Tech Thesis on

Thermal Pyrolysis of Groundnut De-Oiled Cake and Characterization of Bio-Oil Produced

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107CH015

CERTIFICATE

This is to certify that the work in this thesis entitled **"Thermal pyrolysis of groundnut de-oiled cake and characterization of the bio-oil produced"** submitted by **Ankit Agrawalla (107CH015)** in partial fulfillment of the requirements of the prescribed curriculum for Bachelor of Technology in Chemical Engineering Session 2007-2011 in the department of Chemical Engineering, National Institute of Technology Rourkela, Rourkela is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge the matter embodied in the thesis is his bona fide work.

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Ankit Agrawalla

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NOMENCLATURE

MTOE	Million tons of oil equivalents
TERI	The Energy and Resources Institute
GoI	Government of India
GDP	Gross Domestic Product
MNRE	Ministry of New and Renewable Energy
TGA	Thermo-gravimetric Analysis
PID	Proportional-integral-derivative
ASTM	American Society for Testing and Materials
SEM	Scanning Electron Microscope
FTIR	Fourier Transform Infrared Spectroscopy
GCV	Gross Calorific Value

ABSTRACT

Energy crisis have led to a vast research on various alternative sources of energy in order to cope up with the growth in standard of living of all human beings across the world. Biomass is found to be one of the most promising sources of energy which can ease out the energy crisis. Hence, various technologies and processes are evolved to utilize the biomass resource efficiently. Pyrolysis is one of the latest technologies which have the potential to provide valuable liquid and gaseous fuels from these biomass sources. In this paper, thermal pyrolysis of groundnut de-oiled cake was performed in a semi batch reactor at a temperature of 450°C for the production of groundnut pyrolytic oil or the bio-oil. The physical properties analysis of bio-oil was compared with physical properties of commercial transportation fuels and other pyrolytic oils. GC-MS was performed to determine its chemical composition. Kinetic study of the pyrolysis reaction was also done.

Keywords: *Pyrolysis, Groundnut De-oiled Cake, Pyrolytic Oil, Kinetic Study*

INTRODUCTION

1. Introduction

Nowadays, Energy has become a stature symbol for economic growth and human development. It has been observed that energy consumption shows a two way relationship with economic development, one is economy growth which relies on availability of cost effective and environmental friendly energy sources whereas on the other hand, level of economic development which is observed to be reliant on energy demand.

In a growing economy like India, energy is an essential building block of its development. In the past decades, India's energy consumption has been increasing at one of the fastest rates in the world due to rapid population growth and economic development, with its primary commercial energy demand increasing by 6% from 1981 to 2001 as reported by Planning Commission, Government of India[1]. India accounted for 3.5% of the world commercial energy demand in the year 2003 making it fifth highest consumer in the world in terms of primary energy consumption[2]. However, per capita energy consumption in India is still very low compared to other developing/developed countries irrespective of its overall increase in energy demand.

Indian energy sector has witnessed rapid growth and revolutionary developments in areas like resource exploration and exploitation, energy sector reforms and capacity additions in order to meet its demands on its course to become a developed country. Still, India is lagging behind to meet the increasing energy demands because of rapid urbanization, multiplying population and progressing economy even after the efforts made in energy supply growth and resource augmentation. These energy shortages are affecting tremendously to Indian economy as it has to rely heavily on imports.

1.1.Trends in Energy Resources

India has been gifted well enough with both exhaustible and renewable energy resources. Coal, Oil, and Natural Gas are the three primary commercial energy sources on which India has relied upon from decades. Till the end of 1980s, India's energy policy was mainly based on availability of native resources which made coal the largest source of energy. India lacks in oil assets and therefore has to depend on crude imports to meet a major share, around 70% of its needs in 2009 [3]. However, India's primary energy mix has changed a lot over the decades butcoal has remained the most significant & ample fossil fuel in India till now and is expected to be the dominant source for energy till 2030 with a contribution of around 51% of India's energy need[4]. Currently, coal contributes around 52% (283 MTOE) of commercial energy requirements whereas petroleum products accounts for 30-35%, nearly 9 per cent by natural gas and 2% by nuclear and 2% hydro energy [4].

Indian economy relies heavily on commercial fuels but a sizeable quantum of energy requirements, especially in the rural household sector, is met by non-commercial and traditional energy sources such as fuelwood, crop residue, biomass and animal waste,human and draught animal power. The usage of such sources of energy is estimated at around 155 MTOE/annum [5]. However, higher quality and more efficient commercial energy sourceshave started to replace the traditional energy resources.

In Planning Commission 2002, it was desired by Government of India to achieve 10% GDP (Gross Domestic Product) growth rate during Eleventh Five Year Plan and to maintain an average growth rate of about 8% for the next 15 years. It confirmed that country's requirements for energy and supporting infrastructure is going to increase rapidly and in order to facilitate the policy makes to make prompt decisions, estimation of the total energy requirements as well as

look at the economic, environmental, and geopolitical implications of India's alternative energy pathways for the next few decades is very crucial. Demographic profile, change in lifestyle, and consumer preferences determined the level of useful energy demands, whereas the availability, prices of resources and technologies influenced the levels and patterns of final energy requirements in the future[6].

In order to estimate the total energy requirements in future, The Energy and Resources Institute (TERI, Office of the Principle Scientific Adviser, GoI) modeled a system to determine the total commercial energy requirements over the period of 2001-2031 under different scenarios such as BAU (business as usual), REN (aggressive renewable energy), NUC (high nuclear capacity), EFF (high efficiency), HYB (hybrid), LG (low growth), HG (high growth) and HHYB (high hybrid) which almost dictated the routes toward future and increase in energy consumption as the cost for the route. The findings are shown below:

Table 1: Variation in Total Energy Consumption in MTOE (Million Tons of Oil Equivalent)[6]

Scenario	2001/02	2006/07	2011/12	2016/17	2021/22	2026/27	2031/32
BAU	285	391	527	749	1046	1497	2123
REN	285	391	524	740	1033	1479	2097
NUC	285	391	527	749	1030	1455	2061
EFF	285	379	479	623	838	1131	1542
HYB	285	379	478	619	823	1101	1503
LG	285	361	456	605	816	1134	1579
HG	285	435	638	962	1438	2186	3351
HHYB	285	405	544	760	1087	1576	2320

As reported by TERI, the total commercial energy consumption in BAU scenario, is estimated to increase up to 2123 MTOEs, i.e. by 7.5 times, till 2031. A comparative study between effect of different economic growth scenario such as LG (economy grows at 6.7% with

a GDP of 5.9%) and HG (economy grows at 10% with GDP 8.6%) on energy requirements showed that commercial energy requirement will increase to only about 1579 MTOE by 2031 in LG scenario, whereas the energy requirements can be as high as 3351 MTOE in the HG scenario. The REN and NUC scenario analysis also cleared it that the plans of enhancing the exploitation of hydro energy, nuclear energy and renewable energy sources will not help much when compared to total commercial energy requirements by 2031. It was estimated that the contribution of hydro, nuclear, and renewable energy forms together will increase by about 6 times over the period 2001–31, but they can contribute only 4.5% of the total commercial energy requirements. Thus, the dependence on the three conventional energy forms: coal, oil, and gas will continue to remain high for the next few decades. Increase in efficiency in power, industrial and transport sectors, on both demand and supply side, showed a significant scope of reducing overall energy consumption. In the HYB scenario, energy requirements by the year 2031 would be of the order of those in the LG scenario, while those in the HHYB scenario will be in the range of requirements in the BAU scenario.

A fuel wise commercial energy consumption analysis was also made to check the dependence on various fuels. It was seen that, Natural Gas will be a preferred option for power generation and fertilizer production but coal and oil will remain dominant fuels till next few decades. However, the HYB scenario indicates some potential to reduce coal and oil requirements as compared to the BAU scenario only with adequate, timely policy and technological intervention.

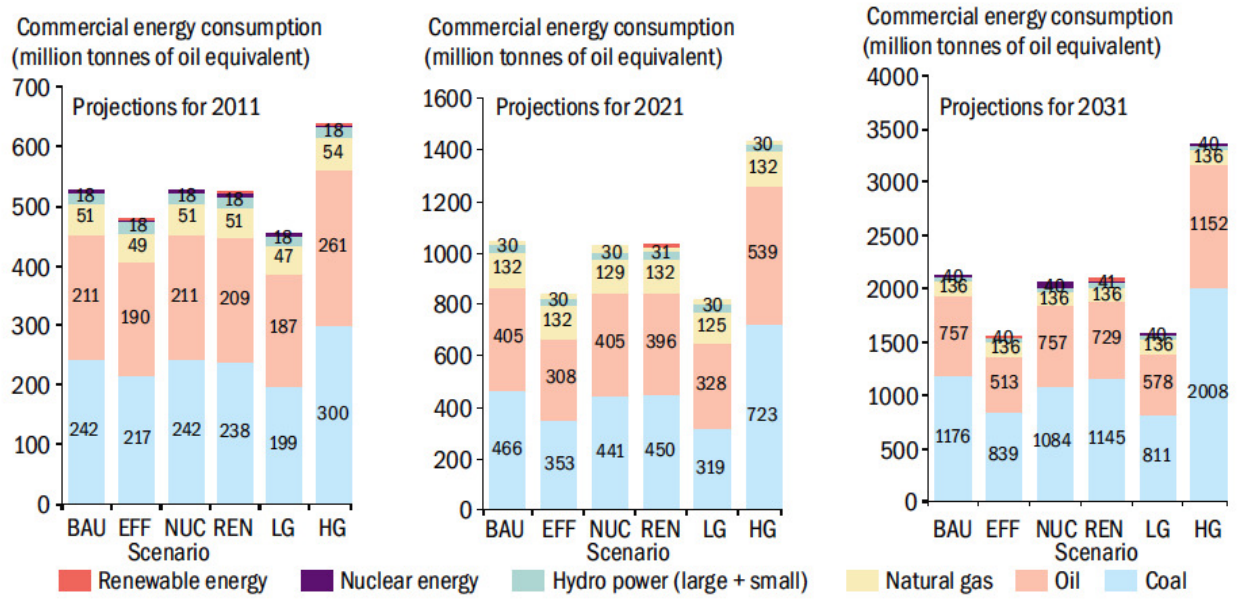

Figure 1: Fuel Wise energy Consumption under various scenarios [6]

The report have clearly shown that in order to reduce dependence on imports of conventional energy fuels and to withstand energy security viewpoint, the country have to undertake every possible options on the demand and supply side simultaneously so as not only to reduce its total energy requirements but also diversify its fuel resource mix. An integrated energy planning exercise with the following key elements were suggested:

- More thrust to exploration and production of coal, involvement of private sector.
- Energy security in hydrocarbons, engage private sector to produce hydrocarbons.
- Reduce coal requirements and consumption of petroleum products, Natural gas to be the preferred fuel.
- Renewable energy resources to be made competitive, and targeted to spread it in remote areas and for decentralized power generation.
- Enhanced efforts to tap alternative indigenous energy sources.
- Reduce transmission and distribution loss.

1.2. Potential for Clean Energy

In current scenario, where the consumption of fossil fuels, in both rural and urban sectors, have increased exponentially over the past decades and is expected to increases in the same manner for next couple of decades will lead to increase in not only its market price but also in the greenhouse gas emissions. Thus, a dire need to put a control over its consumption has been felt by environmentalists and economists as well. In regard to this, a lot of research works are going on around the globe on various alternative sources of energy such as solar energy, wind energy, geothermal energy, hydrogen, nuclear energy, biofuel or biomass, etc.

Renewables have continuously shown enormous potential to meet the growing energy requirements of the increasing population of the developing world along with sustainable solutions to the global threats of climate change. In a country like India, renewable sources have special significance owing to its geographic diversity and size of country and its rural economy. As reported by MNRE in its annual report 2010-11[7], India has a potential of generating 87,200 MW (close to current energy generated by thermal power) of energy from renewable sources like wind power (48,500 MW), small hydropower (15,000 MW) and bio power (23,700 MW - including biomass power, bagasse cogeneration, urban and industrial waste to energy). In respect to solar energy, India can generate 20-30MW per Sq.Km. Now, India has an area of 3.287 million Sq.km., out of which 87.5% is covered by agricultural, forests and fallow lands, 6.7% by housing and industry and rest 5.8% is either barren or snow bound or generally inhabitable, thus making 12.5% of land available for solar installation. If 10% of this land is utilized for solar installations then it can generate 0.82-1.23 million MW of energy.

In India, focus on renewable energy came a bit late in around 1980s, when a commission on Additional Sources of Energy was implemented in 1981 along with a Department of Non-

Conventional Energy Sources in 1982. Renewable energy programmes were also initiated in the country with focus on research and development, demonstration and extension based on grants and subsidies. Various state nodal agencies were also established in order to co-ordinate, implement, and facilitate renewable energy programmes. IREDA (Indian Renewable Energy Development Agency) established in 1987 was a unique institutional innovation which has to take care to finance renewable energy projects. To provide further motivation to renewable energy development and its utilisation; a full-fledged Ministry, the Ministry of Non-Conventional Energy Sources was formed in 1992.During 1990s, the emphasis of renewable energy programmes was shifted on commercialisation and market orientation to encourage greater involvement of the private sector. These programmes are supported by state-level policies for power generation from renewables, including wheeling, banking, and power purchase which led to the creation of a sizable indigenous manufacturing base and an institutional framework and delivery mechanism to support research, development, demonstration, deployment, and extension. As a result of this, till date India has many achievements in several areas in the renewable energy field.

According to MNRE, 18,842 MW of grid connected renewable power was in place till January 31st, 2011 and is expecting to add more 3646 MW by the end 11th Five Year Plan (2007-12). Around 70% of the installed capacity, i.e. 13,184 MW, is supplied by wind power only whereas other contributors are small hydropower (2,953 MW), bio power (2,673 MW) and 32 MW supplied by solar power [7].

1.3. Biomass

Material originated biologically, other than those which got embedded in geological formations and converted to fossils, are referred as biomass. Plants absorb CO_2 from its surrounding and convert it into biomass by photosynthesis. The energy stored in biomass is derived from the solar energy absorbed by plants during photosynthesis. Biomass sources can be generally classified as different kinds of woody and herbaceous plants, fruits, seeds, energy crops and animal or horticulture or industrial by-products. Biomass life cycle indicates a high potential of being a clean energy source as it doesn't add any extra CO_2 to the atmosphere.

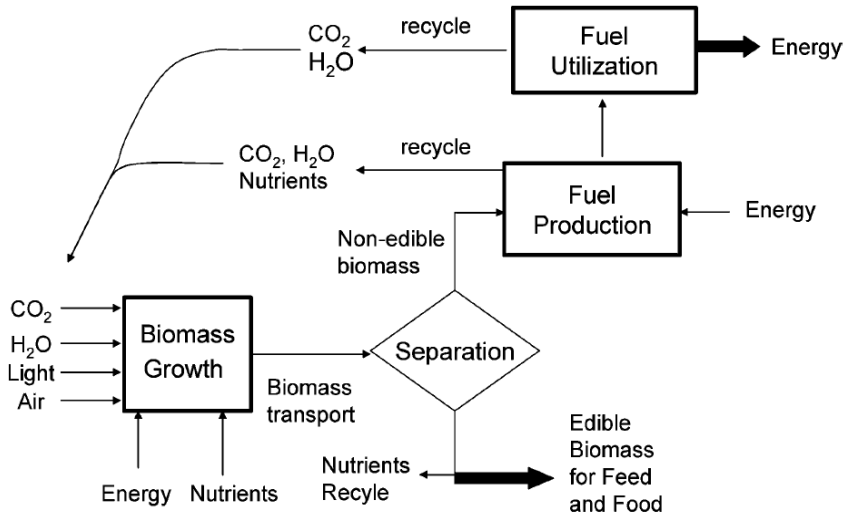

Figure 2: Biomass Life Cycle [8]

Before 19th century, biomass was the primary energy source till the discovery of a liquid fuel, known as crude oil, which industrialised the whole world and improved the standard of living of the people. Eventually, the society became dependent on this crude oil and led to massive exploitation of all crude oil resources and negligence in development of other energy sources for almost two centuries. Such an attitude has resulted into energy crisis situation after the extinction of crude oil resources. Owing to this, all countries have changed their focus back to renewable energy in order to achieve a sustainable world energy matrix. Among the renewable

energy sources, biomass has been stressed more as it is available in abundance, is easy to culture and has a comparatively lower market value. Moreover, the technologies required for its conversion are very basic and well established. They just need to be nurtured in order to increase their efficiency and credibility of biomass. It has also been observed that if biomass is utilized properly then it can supplement 10-14% of world's total energy. In ancient period, energy from biomass was extracted by direct combustion which was very inefficient and polluting due to its high moisture content and low density. Nowadays, a lot of modifications and pre-treatment of biomass have resulted into various efficient technologies. The advanced technologies are more focused on converting biomass into secondary energy forms such as electricity, gaseous and liquid fuels, hydrogen, etc. There are basically three principal methods of conversion of biomass: (a) Thermo-Chemical Conversion, (b) Physical-Chemical Conversion and, (c) Bio-Chemical Conversion.

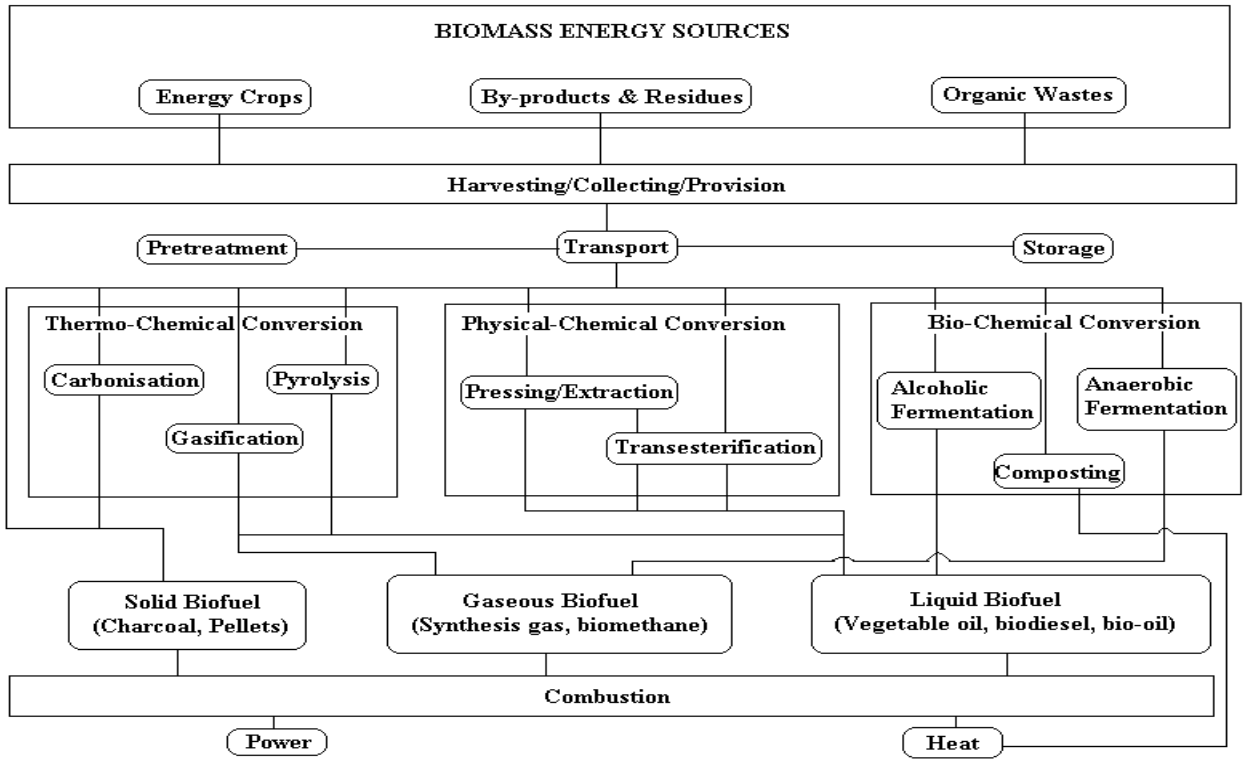

Figure 3: Principal Methods of Biomass Conversion [9]

As it can be observed, these conversion processes yield biofuels in all the three physical forms of matter:

i. Solids: charcoal, pellets, etc.

ii. Liquids: vegetable oil, biodiesel, pyrolytic oil or bio-oil, bioethanol, etc.

iii. Gaseous: synthesis gas, mixtures of hydrocarbons gases with CH_4 and CO, etc.

1.4. Pyrolysis

Pyrolysis is a thermo-chemical process for conversion of biomass by heating the biomass feedstock at high temperature in absence of air which produces gaseous products which is then condensed to give liquid fuels consisting of pyrolytic oil or bio-oil and oily water (mixture of water and certain hydrocarbons). Almost 70-80% of gaseous products are converted in liquid fuels providing a good quantity of liquid fuel which then can be enhanced according to its use. The reason for popularity of this process is that it derives a good quantity of liquid fuel, from biomass, which has properties very close to commercial transportation fuels and hence can be upgraded or modified to replace transportation fuel. Moreover, it also provides some amount of gaseous and solid products which have higher market value as they can also be used as a source of energy.

1.5. Pyrolysis of De-Oiled Seed Cakes

In the quest for a liquid fuel which can have the potential to replace transportation fuel, a lot of researches are being carried out in ever corner of the world. Apart from biodiesel and bio-ethanol which are obtained from esterification or fermentation, pyrolytic oils obtained by pyrolysis of biomass have provided good results to diverge some attention towards it. Although origin of the raw material for producing biodiesel, bioethanol and pyrolytic oil is same, but they cater different uses and market value. Biodiesel or bioethanol are prepared using oils extracted

from energy crops or edible seeds along with certain chemicals, which indicates that they are using raw materials having other meaningful utilities and higher market value. In a country like India, where lot of people are struggling for minimal diet, utilizing edible oils extracted from oilseeds for production of bio-diesel is not justified to mankind. Thus raw material resources available for bio-diesel production limits to specifically cultivated non-edible energy crops. Now, pyrolytic oil can be obtained from any of the agricultural and industrial residues and wastes such as de-oiled cakes, plastics, bagasse, rice husk, etc. which are treated as scrap. Therefore, the raw material used is not only cheap but also doesn't have any better use than this.

So, abundantly available cheap raw material which are being mostly treated as scrap when pyrolysed produces a liquid fuel which shows a quite admissible properties for being a commercial fuel; a certain thing which every country is looking forward to. Thus, a lot of researches have been carried out on pyrolysis of de-oiled cakes with different raw materials such as rapeseed[15], [18] ,[19], [20], cottonseed[23], safflower[11], [12], [14], [22], sunflower[21], olive oil residual cake[13], cherry seeds[17], rice husk[16], bagasse[25] and even on fruit pulps[24] and energy crops[10].

In most of the researches, people have obtained pyrolytic oil and characterized its physical properties such as density, viscosity, flash point, pour point, calorific value, distillation boiling range to check its feasibility as transportation fuel. They have also analyzed all the chemical compounds present in the oil via chromatograms, spectroscopy, etc. to gain an insight on its stability, volatility and corrosive nature.

After physical and chemical characterization, some of researchers have studied the kinetics of the reactions taking place and have modeled the rate equation and determined activation energy of the reaction.

1.6. Pyrolysis of Groundnut De-Oiled Cake

According to World Market and Trade Analysis, Groundnut is the fourth largest oilseed produced in the world after Soybean, Rapeseed/Mustard and Cottonseed accounting for around 34.71 million metric tons produced in the fiscal year April 2010/11. *Indian Oilseeds and Produce Exports Promotion Council* [26] have analyzed that around 5.12 million tons of groundnut was produced during the year 2009-10 making it third largest produced oilseed of India after Soyabean and Rapeseed/Mustard. Thus, its abundance in quantity can make it a vital source for biomass in a developing country like India. Irrespective of groundnut being available in plenty of quantity, very little work has been carried out on it.

Therefore, in this paper, pyrolytic oil is obtained by pyrolysis of groundnut de-oiled cakes and has been characterized for its chemical and physical properties. Its properties were compared with those of commercial transportation fuels and other pyrolytic oils. Activation energy for the process is also determined using thermo-gravimetric analysis of the sample.

MATERIALS

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METHODS

2. Materials and Methods

2.1. Raw Material

The groundnut de-oiled cake used in the experiment was bought from a fodder shop from a local market of Rourkela, Orissa, India. The cake was in the form of flakes and was powdered, using a household grinder, before use so as to minimize voids inside the reactor as well as to fill maximum amount of cake into the reactor.

2.2. Thermo-Gravimetric Analysis

Pyrolysis is heating of a substance in absence of air at a particular temperature. Therefore, the temperature for effective pyrolysis of the groundnut cake has to be determined. For this purpose, thermo-gravimetric analysis (TGA) of the sample cake was done using a DTG60 instrument. Around 20-30 milligrams of sample cake was taken and heated up to a final temperature of 800°C and a residence time of 1 minute at 800°C was allowed. TGA was performed both in air and nitrogen atmospheres at a heating rate of 25°C/Min and one observation was taken at a heating rate of 20°C/Min in air medium. Thermo-gravimetric weight loss curve was plotted against temperature. It provides a range of temperature in which maximum thermal degradation of groundnut de-oiled cake takes place.

2.3. Experimental Procedure

It consisted of a reactor-furnace system in which the furnace temperature was maintained constant using a PID controller. At the outlet of reactor, a condenser was attached to condense the vapors coming out of it. The condensed liquid was collected in a collecting jar at the end of condenser. The de-oiled cake is filled in a reactor of 300 ml and the reactor is kept in the furnace for heating at constant temperature, temperature at which maximum yield of liquid product is obtained. When the reaction starts, vapors coming out of reactor through the provided outlet are

condensed in a condenser as shown in figure 4. Water is circulated as cooling medium in the condenser via a pump. The condensed vapors are collected in a container as the liquid product whereas there is some amount of non-condensable gases which are simply left out. The liquid product collected contains oily water and bio-oil. Oily water is basically water with some dissolved hydrocarbons. Oily-water and bio-oil is further separated by difference in their density.

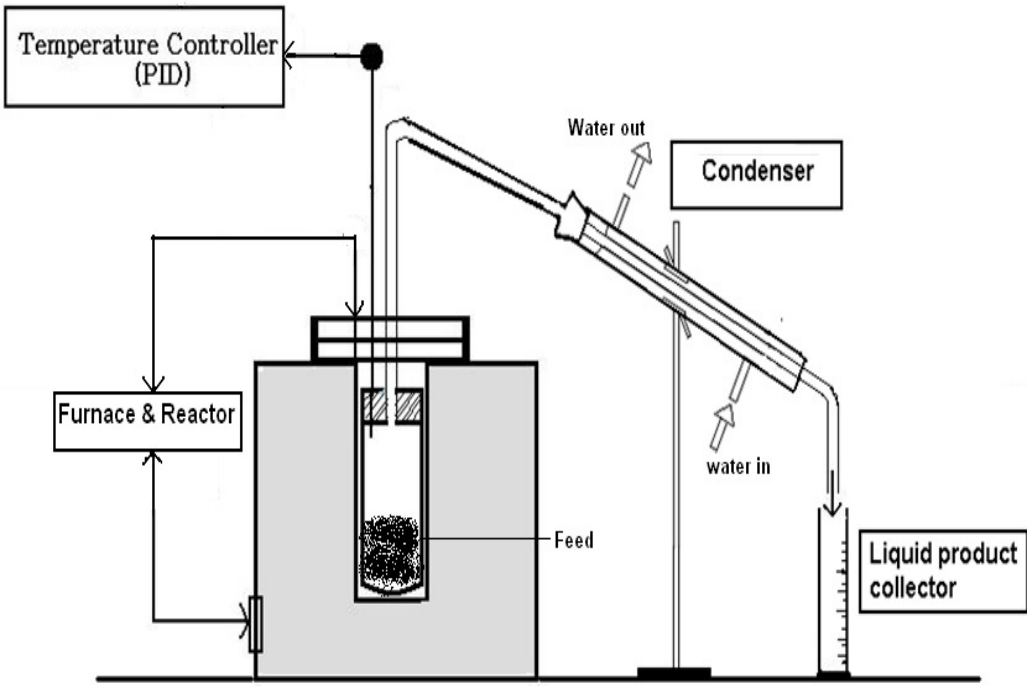

Figure 4: Experimental Set-Up

2.4. Sample Pyrolysis Runs

Once the temperature range was found out then sample pyrolysis runs were done with 30gms of cake in that range at intervals of 50°C to determine the temperature at which maximum yield of liquid product is obtained. During sample runs various data like reaction time, yield of char, and yield of liquid product were noted down. Variation in yield of char, liquid product and gas (volatiles) with respect to temperature is plotted. Variation in reaction time with temperature was also plotted.

2.5. Characterization of Raw Material and Char

The groundnut cake and char were analyzed in order to observe the change in the properties of the solid material as a result of pyrolysis.

2.5.1 Proximate Analysis

It provides information on moisture content, ash content, volatile matter content and fixed carbon content of the material. It was carried out using *ASTM D3172 - 07a* [27] method.

2.5.2. Ultimate Analysis

Ultimate analysis is performed to determine the elemental composition of the material. It was carried out using a CHNSO elemental analyzer (Variael CUBE Germany) which provides carbon, hydrogen, nitrogen, sulphur percentage composition. And when sum of theses compositions is subtracted from 100, it gives oxygen percentage composition.

2.5.3. Calorific Value

Calorific value of a material is the amount of heat liberated when 1Kg of that material is burnt. It was determined for both cake and char using a bomb calorimeter (Model: AC-350, LECO Corporation, USA).

2.5.4. Oil Content

Oil content of the raw material was found out using Soxhlet apparatus.

2.5.5. Surface Area of Char

2.5.5.1. BET

The surface area of the char obtained was determined, to investigate it utility as an adsorbent, using a Surface Area Analyzer (Model: Smartsorb 92/93), Smart Instruments, Mumbai.

2.5.5.2. SEM

The surface of the char obtained was viewed under a Scanning Electron Microscope (Model: JEOL-JSM-6480LV SEM) at different magnification values to have a clear view on pore density and size.

2.6. Physical Characterization of Bio-Oil

Physical properties such as density, specific gravity, viscosity, conradson carbon, flash point, fire point, pour point, cloud point, calorific value, sulphur content, distillation boiling range and cetane index of the bio-oil was determined using the following standard methods:

Table 2: Standard Methods for Physical Property Analysis

Physical Property	Method
Density	ASTM D1298 - 99
Kinematic Viscosity	ASTM D445 - 11
Conradson Carbon	ASTM D189 - 06(2010)e1
Flash Point	ASTM D6450 - 05(2010)
Fire Point	ASTM D1310 - 01(2007)
Pour Point	ASTM D5853 - 09
Calorific Value	ASTM D5468 - 02(2007)
Distillation Boiling Range	ASTM D2887 - 08
Cetane Index	ASTM D4737 - 10

2.7. Chemical Characterization of Bio-Oil

2.7.1. FTIR

In order to determine the functional groups present in the pyrolytic oil, Fourier Transform Infrared spectroscopy of the oil was analyzed in a Perkin-Elmer infrared spectrometer.

2.7.2. GC-MS

Gas Chromatography – Mass Spectrometry of the pyrolytic oil was performed using a GC-MS-OP 2010[SHIMADZU] analyzer in Sargam Laboratory, Chennai to determine the chemical compounds present in the oil.

RESULTS

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DISCUSSION

3. Results & Discussion

3.1. Thermo-Gravimetric Analysis

The TGA curve showed that the maximum thermal degradation of the cake took place in the temperature range of 200-500°C in all the three observations. In nitrogen medium, a second temperature range of 500-650°C is observed for thermal degradation of the cake but the vapors obtained during this phase are generally higher hydrocarbons and are non-condensable. Thus temperature range of 500-650°C was neglected as it will not increase the yield of liquid product which is the main concern out here.

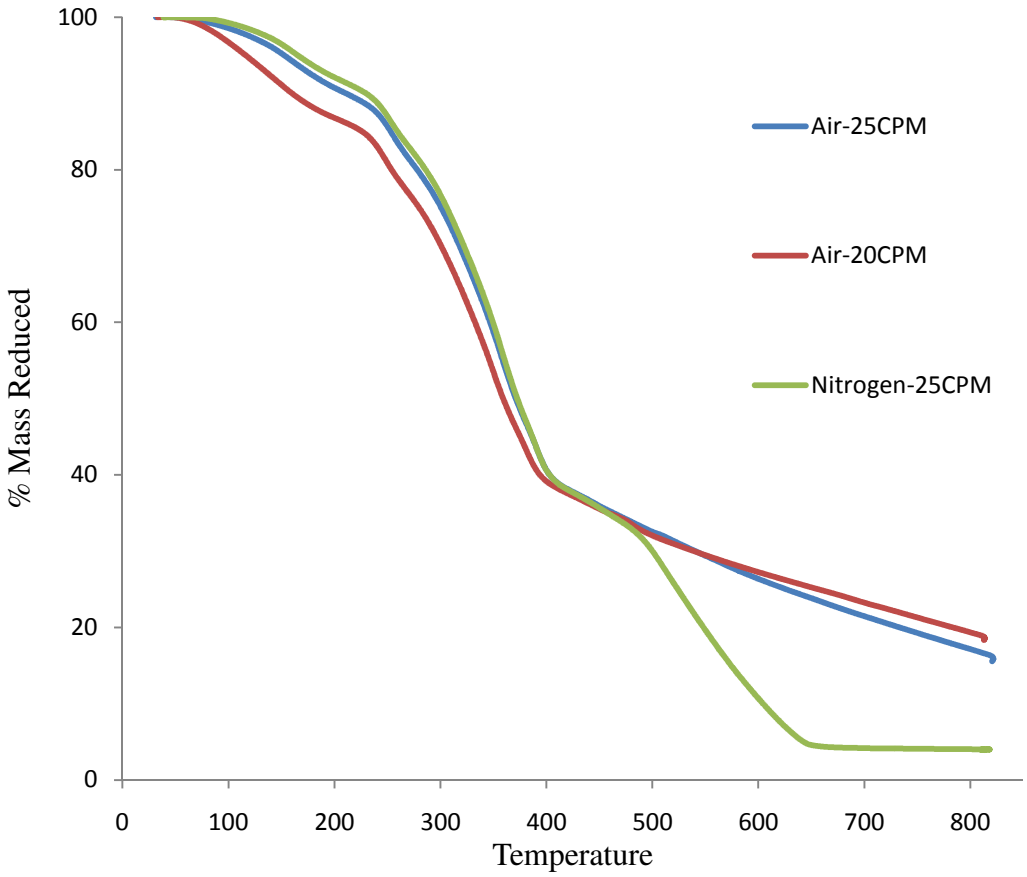

Figure 5: TGA Curve for Groundnut De-Oiled Cake

3.2. Sample Pyrolysis Runs

The plot between yield of liquid, solid and gaseous products vs. temperature clearly shows that the yield of liquid product increases with increases in temperature in the range of 200-500°C up to 450°C and then it starts decreasing. Thus maximum yield of liquid product is obtained at 450°C which indicates it as effective pyrolysis temperature for groundnut de-oiled cakes. Reaction time decreases with increase in temperature.

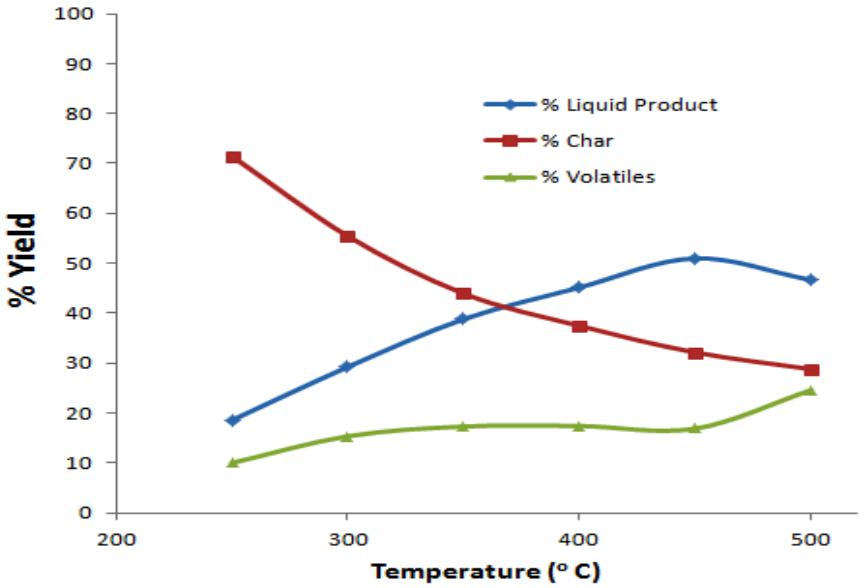

Figure 6: Yield vs. Temperature

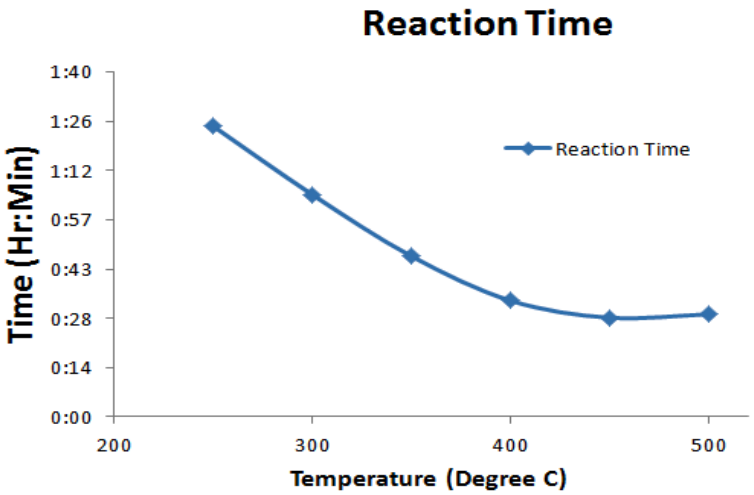

Figure 7: Reaction Time vs. Temperature

3.3. Characterization of Groundnut De-Oiled Cake and Char

Proximate analysis is the quickest and simplest way of investigating the fuel quality of solid materials. High moisture content effects the conversion efficiency and heating value of biomass and have a potential to loose energy during storage as a result of decomposition. Higher value of ash content also affects heating value. High volatile content indicates that the material is more volatile than solid fuels whereas loss in fixed carbon content during pyrolysis should be less. The de-oiled cake has a very high volatile matter content of 83% which reduces drastically to 35.3% after pyrolysis which indicates higher conversion of biomass to liquid fuels. As a result of decrease in volatile matter content, fixed carbon of material increased significantly which means there is less liberation of fixed carbon.

Ultimate analysis showed significant variation in carbon and oxygen content whereas there were slight variations in hydrogen, nitrogen and sulphur content.

Table 3: Groundnut De-Oiled Cake and Char Characterization

	Groundnut Cake	Groundnut Char
Moisture Content	5.6	4.08
Volatile Content	83	35.3
Ash Content	4.8	15.6
Fixed Carbon	6.6	45.02
C	46.37	63.78
H	7.015	3.94
N	6.89	7.58
S	0.287	0.167
O	39.438	24.533
C/H Molar Ratio	0.55	1.35
C/N Molar Ratio	7.851717465	9.816622691
% Oil Content	4.18	-
Empirical Formula	$C_{7.85}H_{14.25}O_{5.01}NS_{0.02}$	$C_{9.82}H_{7.28}NO_{2.83}S_{0.01}$
Gross Calorific Value(MJ/Kg)	15	25.16
Surface Area(m^2/gm)	-	0.59

3.3.1. SEM Images

The images of the char surface obtained from scanning electron microscope (SEM) at magnification levels of 500, 2000 and 8,500 clearly shows reasonable amount of pores present on the surface.

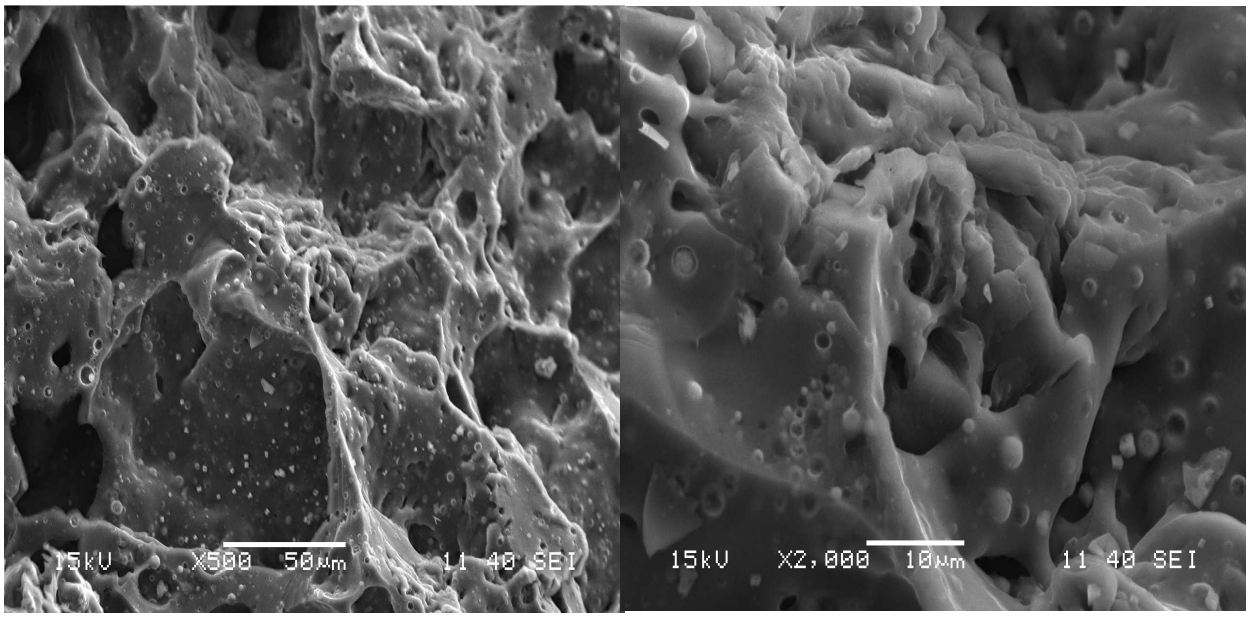

Figure 8: SEM Images of Char Surface: 500 magnifications (left) and 2000 magnifications (right)

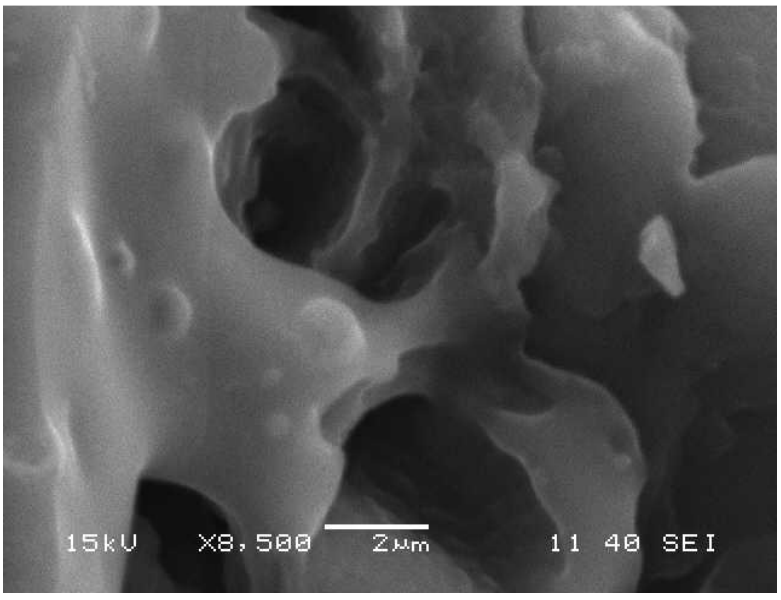

Figure 9: SEM Image of Char Surface at 8,500 magnifications

3.4. Physical Properties of Bio-Oil

Table 4 shows the physical properties such as density, specific gravity, kinematic viscosity, carbon residue, sulphur content, flash point, fire point, pour point, cloud point, gross calorific value, distillation boiling range and cetane index which helps in assessing and determining feasibility of bio-oil as commercial liquid fuels.

Table 4: Physical Properties of Bio-Oil

Products Properties	Groundnut Pyrolytic Oil
Density @ 15°C in gm/cc	1.0219
Specific Gravity @ 15°C/15°C	1.0228
Kinematic Viscosity @ 40°C in CSt	44.9
Conradson carbon residue (%)	4.09
Flash Point (°C)	50
Fire Point (°C)	62
Cloud Point (°C)	3
Pour Point (°C)	-2
Gross Calorific Value in Kcals/kg	6917
Sulphur Content (%)	0.5
Distillation:	
Initial boiling Point (°C)	90
10% Recovery (°C)	98
30% Recovery (°C)	250
50% Recovery (°C)	312
70% Recovery (°C)	342
90% Recovery (°C)	358
Final Boiling Point (°C)	362
Calculated Cetane Index (CCI)	22

From comparison of physical properties of bio-oil with transportation fuels [Table 5] it can be observed that groundnut bio-oil is more dense and highly viscous which may affect pumping and injection of fuel in the engine at lower temperatures. Density and viscosity of bio-oil can be modified by blending it with different transportation fuels. Flash point of bio-oil is in

comparable range and hence will ensure safe storage but pour point is minus 2°C which will not cause any trouble in most of the regions but in colder regions with sub zero climate it may have freezing problems. Calorific value is around 70% of that of gasoline and diesel which is actually good enough for an agricultural waste although we will have somewhat less performance of engine. The distillation range showed that the bio-oil starts boiling at 90°C and the distillation stops at around 360°C. It means the bio-oil contains substantial amount of volatiles as it initial boiling point is below 100°C. Only 2-3% of the bio-oil is found as residue at the end of distillation. As it can be observed from Table 4, the properties of bio-oil were in similar range to that of other pyrolytic oils.

Table 5: Comparison of Fuel Properties

Properties / Fuels	Specific Gravity $15^oC/15°C$	Kinematic Viscosity @40^oC (cSt)	Flash Point	Pour Point	GCV (MJ/Kg)	IBP	FBP	Chemical Formula
Groundnut Pyrolytic Oil	1.0228	44.9	50	-2	28.9	90	362	C_4-C_{28}
Gasoline[29]	0.72-0.78	-	-43	-40	42-46	27	225	C_4-C_{12}
Diesel[28]	0.82-0.85	2-5.5	53-80	-40 to -1	42-45	172	350	C_8-C_{25}
Bio-Diesel[28]	0.88	4-6	100-170	-3 to 19	37-40	315	350	C_{12}-C_{22}
Heavy Fuel Oil[25]	0.94-0.98	>200	90-180	-	40	-	-	-
Rapeseed[18-20] Pyrolytic Oil	0.993	>40	62	6	36-37	-	-	$CH_{1.78}N_{0.04}O_{0.15}$
Safflower[11, 12, 14] Pyrolytic Oil	1.02-1.079	50-250	58-76	-16	38-41	92	315	$CH_{1.88}O_{0.15}N_{0.02}$
Grape Bagasse[25]	0.992	>23	61	-	32.95	-	-	$CH_{1.45}O_{0.17}N_{0.03}$
Olive Bagasse[13]	1.07	>50	77	-	31.6	-	-	-

3.5. Chemical Composition of Bio-Oil

3.5.1. FTIR Analysis

FTIR analysis suggests that the functional groups like alcohols, ketones, carboxylic acids, esters, alkanes, alkenes, alkynes, amide, nitriles, nitro compounds, ethers, aromatic rings may be present in the bio-oil. It has to be confirmed with gas chromatography results.

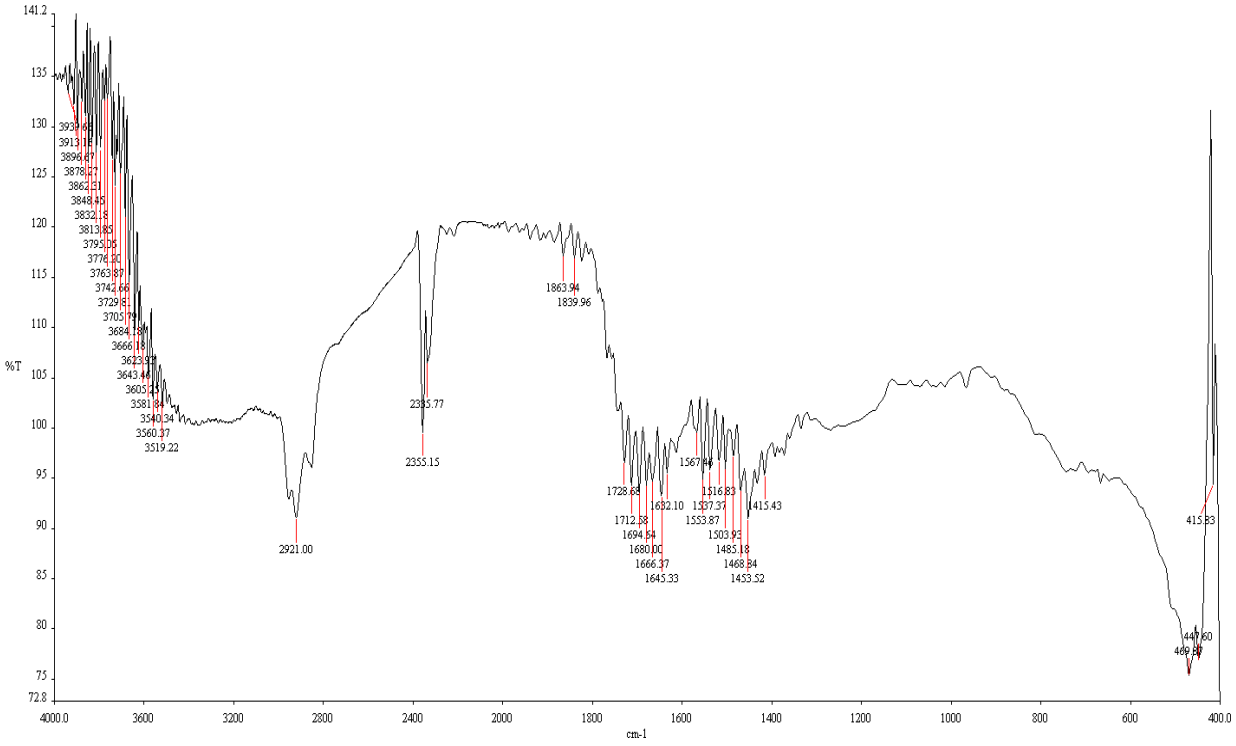

Figure 10: FTIR Graph

Table 6: FTIR Compound and Frequency Table

Compound Type	Frequency
Alkanes	2850-2960
Alkenes	1640-1680
Alkynes	2100-2260
Aldehydes, Ketones, Carboxylic Acids, Esters	1670-1760
Amines	1580-1650
Nitriles	2220-2260
Nitro Compounds	1500-1660
Aromatic Rings	1500-1600

3.5.2. Gas Chromatography-Mass Spectrometry

The chemical composition of the bio-oil was determined using GC-mass spectrometry. The compounds present in the bio-oil were identified by comparing the chromatogram obtained with standard chromatogram data available. It was found that bio-oil consisted of around 70 compounds as shown below [Table 7].

Table 7: Chemical Composition of Bio-Oil

Compound	Area %	Formula
o-Cresol	1.14	C_7H_8O
p-Cresol	4.75	C_7H_8O
o-Guaiacol	1.6	$C_7H_8O_2$
Undecane	0.52	$C_{11}H_{24}$
Butanamide, 3-methyl-	0.46	$C_5H_{11}NO$
3-pyridinol	2.93	C_5H_5NO
Hexanamide	1.24	$C_6H_{13}NO$
2-methyl-3-hydroxypyridine	0.63	C_6H_7NO
2-ethylphenol	0.86	$C_8H_{10}O$
Succinimide	0.27	$C_4H_5NO_2$
Benzyl nitrile	0.48	C_8H_7N
2,4-dimethylphenol	1.03	$C_8H_{10}O$
Glutarimide	1.32	$C_5H_7NO_2$
4-ethylphenol	2.41	$C_8H_{10}O$
1-acetylpyrrolidine	0.41	$C_6H_{11}NO$
3,3-Dimethylpyrrolidine-2,5-dione	0.28	$C_6H_9NO_2$
(3z)-3-tetradecene	0.28	$C_{14}H_{28}$
Dodecane	1.38	$C_{12}H_{26}$
2,3-dihydro-benzofuran	0.44	C_8H_8O
3-phenylpropionitrile	0.98	C_9H_9N
p-Ethylguaiacol	0.94	$C_9H_{12}O_2$
α-Tridecene	0.62	$C_{13}H_{26}$
n-Tridecane	0.91	$C_{13}H_{28}$
Indole	3.16	C_8H_7N
5,5-dimethylhydantoin	1.01	$C_5H_8N_2O_2$
(3z)-3-hexadecene	0.42	$C_{16}H_{32}$
n-Tetradecane	0.91	$C_{14}H_{30}$
β-Methylindole	1.06	C_9H_9N
5-ethyl-5-methylhydantoin	0.51	$C_6H_{10}N_2O_2$

Compound	Area %	Formula
(Z)-2-decenal	0.24	$C_{10}H_{18}O$
5-Isopropyl-2,4-imidazolidinedione	1.17	$C_6H_{10}N_2O_2$
Pentadecane	1.6	$C_{15}H_{32}$
1-heptadecene	0.79	$C_{17}H_{34}$
Heptadecane	1.4	$C_{17}H_{36}$
(8e)-8-heptadecene	0.69	$C_{17}H_{34}$
9-octadecene, (e)-	0.77	$C_{18}H_{36}$
Nonadecane	1.43	$C_{19}H_{40}$
n-Octadecane	1.03	$C_{18}H_{38}$
Tricosane	0.69	$C_{23}H_{48}$
Hexadecanenitrile	2.92	$C_{16}H_{31}N$
Methyl palmitate	0.8	$C_{17}H_{34}O_2$
3-Isobutylhexahydropyrrolo[1,2-a]pyrazine-1,4-dione	0.89	$C_{11}H_{18}N_2O_2$
Octadecane	0.6	$C_{18}H_{38}$
(Z)6,(Z)9-Pentadecadien-1-ol	0.66	$C_{15}H_{28}O$
Oleanitrile	9.24	$C_{18}H_{33}N$
Methyl elaidate	2.83	$C_{19}H_{36}O_2$
Cetyl cyanide, N-HEPTADECANONITRILE	2.48	$C_{17}H_{33}N$
Methyl stearate	0.17	$C_{19}H_{38}O_2$
Bicyclo[4.1.0]hept-3-ene, 7,7-dimethyl-3-vinyl-	0.27	$C_{11}H_{16}$
Palmitamide	4.7	$C_{16}H_{33}NO$
n-Octadecane	0.33	$C_{18}H_{38}$
n-Methyldodecanamide	1.38	$C_{13}H_{27}NO$
Cyclopentane, 1,1'-[4-(3-cyclopentylpropyl)-1,7-heptanediyl]bis-	0.2	$C_{25}H_{46}$
n,n-Dimethyldodecanamide	0.16	$C_{14}H_{29}NO$
(Z)-9-tetradecenal	0.31	$C_{14}H_{26}O$
n-Pentadecane	0.4	$C_{15}H_{32}$
Nonadecanenitrile	0.54	$C_{19}H_{37}N$
Oleic acid amide	14.9	$C_{18}H_{35}NO$
Stearic acid amide	1.86	$C_{18}H_{37}NO$
n-Methyloctadecanamide	3.21	$C_{19}H_{39}NO$
Nonadecanenitrile	1.14	$C_{19}H_{37}N$
Erucylamide	0.19	$C_{22}H_{43}NO$
Lauramide	0.43	$C_{12}H_{25}NO$
Eicosanenitrile	0.99	$C_{20}H_{39}N$
1-[(9E)-9-Octadecenoyl]pyrrolidine	0.6	$C_{22}H_{41}NO$
Myristamide	0.74	$C_{14}H_{29}NO$
4.alpha.,5-cyclo-a-homo-5.alpha.-cholestan-6-one	0.52	$C_{28}H_{46}O$
Stigmast-5-en-3-ol, oleat	0.79	$C_{47}H_{82}O_2$

In chemical composition analysis, it has been observed that although the bio-oil contains around 70 compounds, it mainly consisted of 14.9% Oleic acid amide, 9.24% Oleanitrile, 4.75% p-Cresol, 4.7% Palmitamide, 3.21% N-Methyloctadecanamide and 3.16% Indole accounting for around 40% of total mass. As it can be observed the bio-oil contains compounds with carbon chain length in the range of C_4-C_{28} which is similar to most of fuels used.

KINETIC STUDY

4. Kinetic Study of Reaction

Kinetic analysis of a process can provide information on effect of process parameters on feedstock conversion. Researchers [30-34] have investigated biomass pyrolysis and found that it can be modeled like a cellulose pyrolysis but since it contains polymers of cellulose, hemicellulose and lignin so it may vary according to biochemical composition. It has also been stated that pyrolysis cracking can be modeled as 1st order rate equation as:

$$A\ (Solids) \rightarrow B\ (Solid) + C\ (Volatiles) \quad (1)$$

For 1st order reaction, we have:

$$dx/dt = K(1-x) \quad (2)$$

Where,

$$K = K_o * \exp(-E/RT) \quad (3)$$

&

$$x = (w_i - w)/(w_i - w_f) \quad (4)$$

So,

$$dx/dt = K_o * \exp(-E/RT) * (1-x) \quad (5)$$

Taking heating rate (β) into account;

$$dx/dt = (K_o/\beta) * \exp(-E/RT) * (1-x) \quad (6)$$

Now taking care of effect of variation of temperature on conversion (x), the following equation has been modeled to represent the pyrolysis reaction:

$$Ln(-Ln(1-x)) = Ln((K_o RT^2)/(\beta E)) - (E/RT) \quad (7)$$

Activation energy (E) for the reaction can be obtained from the slope of the linear plot Ln(-Ln(1-x)) versus 1/T using TGA data.

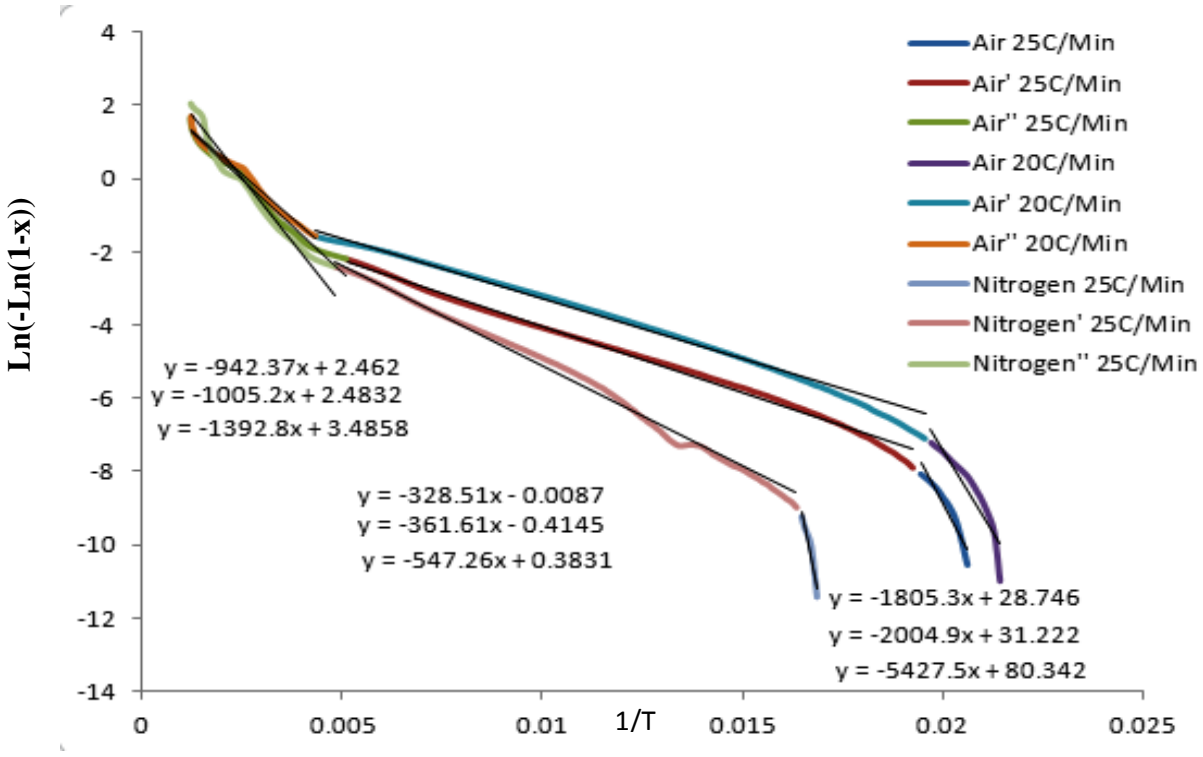

Figure 11: Kinetic Analysis Plot for Determination of Activation Energy

Table 8: Activation Energy for Pyrolysis of Groundnut Cake

Sample	Activation Energy (KJ/Mol)		
	1st Phase	2nd Phase	3rd Phase
N_2 25°C/min	45.12	4.55	11.58
Air25°C /min	16.67	3.01	8.36
Air20°C /min	15.01	2.73	7.83

The reason behind kinetic study of pyrolysis reaction is to determine activation energy for the reaction which implicates the ease of occurrence of reaction. Reactions having less activation energy take place much easily than reaction with high activation energy. A research[32] has shown that pyrolysis of HDPE (High Density Polyethylene) have high activation energy as compared to that of pyrolysis of Jatropha (JC) and Karanja (KP). And when a mixture of HDPE and Jatropha is pyrolysed in 1:1 ratio, the activation energy for such reaction has decreased a lot. It means HDPE can be easily pyrolysed with 1:1 blend of Jatropha. Similar observation has been experienced for pyrolysis of HDPE and Karanja mixture in 1:1 ratio. Thus, biomass feed stocks

having less activation energy for its pyrolysis reaction can be used as a blend to pyrolysis biomass feed stocks with higher activation energy. Activation energy for groundnut pyrolysis is comparably low and hence can be used as a blend.

INDUSTRIAL

SCALE-UP

&

ECONOMIC

ASSESSMENT

5. Industrial Scale-Up and Economic Assessment

5.1. Aim

Designa unit producing Groundnut Pyrolytic Oil by thermal pyrolysis of Groundnut De-Oiled Cake.

5.2. Raw Material

Groundnut De-Oiled Cake

5.3. Products

1. Groundnut Pyrolytic Oil → Used as Bio-Fuel
2. Fuel Gas → Non-Condensable Vapours having high calorific value.
3. Char → Source of Activated Carbon. Also used as Fuel.
4. Oily Water → Contains various hydrocarbons which can be extracted and sold.

5.4. Process

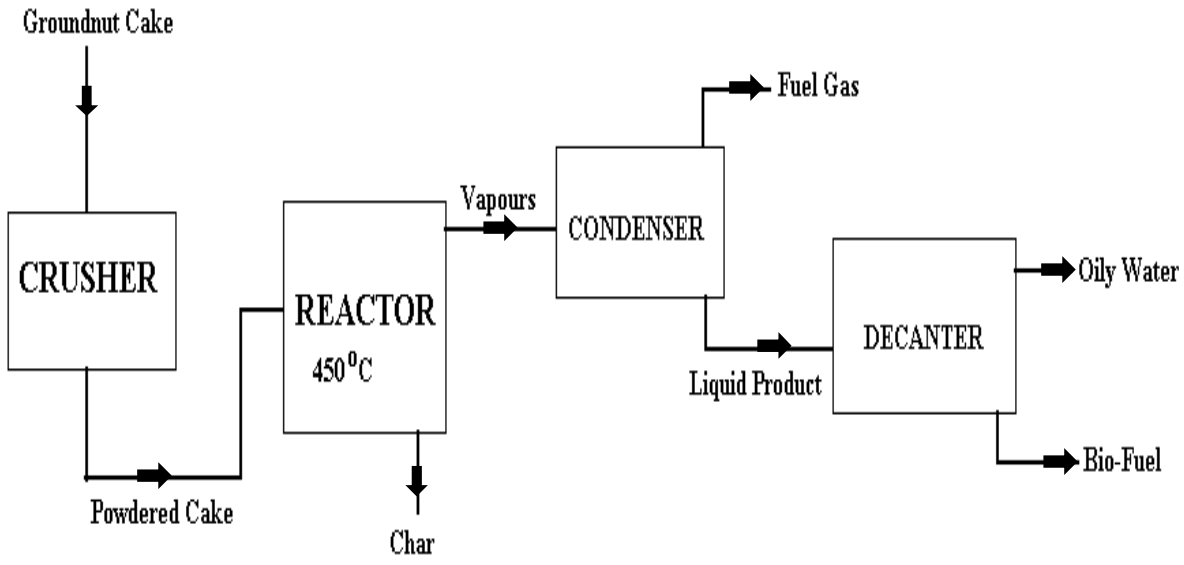

Figure 12: Process Flow Diagram for Pyrolysis Unit

5.5. Material Balance (1Kg Basis)

1 Kg Groundnut De-Oiled Cake ➔ 0.3216 Kg Char

➔ 0.1686 Kg Non-Condensable Vapors (Fuel Gas)

➔ 0.2209 Kg Bio-Fuel

➔ 0.2889 Kg Oily Water

Let us design the unit to process 12 tons of groundnut de-oiled cake in a single run.

So, 12 tons Groundnut De-oiled Cake ➔3859.2 Kg Char

➔2023.2 Kg Fuel Gas

➔2650.8 Kg Bio-Fuel

➔3466.8 Kg Oily Water

5.6. Energy Balance

5.6.1. Energy Balance for Reactor

Pyrolysis of biomass is a very complex process as a lot of reaction takes place simultaneously making it very difficult to optimize energy in a detailed manner. Thus, for the sake of convenience, overall energy required for pyrolysis of different amount of groundnut de-oiled cake was obtained by connecting an energy meter across the furnace. A linear relation was found out from the plot of Mass vs. Energy Consumed.

Table 9: Energy-Mass Analysis

mass (gms)	Q (KJ)
40	2520
50	2556
60	2592
70	2628
80	2664
90	2700

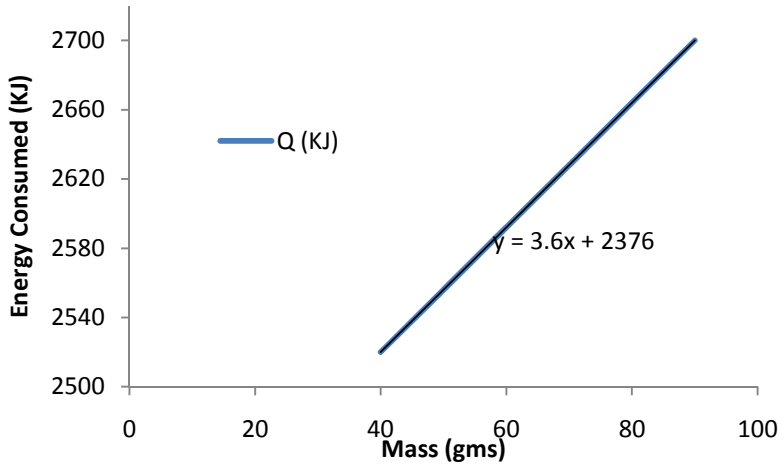

Figure 13: Mass-Energy Consumption Plot

Now using the linear relation, a rough estimation of energy required for pyrolysis of 12 tons of de-oiled cake was found out to be 43,000MJ. This energy is the amount of overall energy consumed by the process, i.e. energy to raise temperature of de-oiled cake from 60°C to 450°C along with energy consumed for pyrolysis reaction, whereas in industry the case will be different. Although the process is a semi-batch process but the furnace won't be allowed to cool down to room temperature after every run as it will cost a lot of energy loss. So, energy consumed is expected to be less than 43,000MJ. Since it is a rough estimation, so calculation are done with 43,000MJ only.

5.6.2. Energy Balance for Condenser

The vapors coming out of reactor is expected to be at around 400°C as the operating temperature is 450°C.

Now,

$$(Vapors\ from\ Reactor) = (Fuel\ Gas) + (BioFuel) + (Oily\ Water) \quad (8)$$

So, input for condenser = 8140.8 Kg Vapors

In this, there are 2023.2 Kg of Non-condensable Vapors (termed as Fuel Gas) and 6117.6 Kg condensable liquid product in which 2650.8 Kg Bio-Fuel and 3466.8 Kg Oily Water. Here also a very rough estimation has to be done in order to determine energy recovered while condensing. Here, the process is condensation of mixture of hydrocarbon vapors. In order to evaluate the energy recovered during condensation and design the condenser mole fraction of each component of hydrocarbon vapor mixture is required with their specific heat capacity, thermal conductivity, viscosity, heat of vaporization, etc. which are not available. So, in this estimation, the hydrocarbon vapor mixture is considered as a single component hydrocarbon vapor with specific heat of vapor as 0.5 KJ/Kg K since it varies in the range of 0.5-3 KJ/Kg K for hydrocarbon vapors at constant pressure. Properties of oily water is also unknown and thus taken same as water, i.e. specific heat = 4.186 KJ/Kg K; latent heat of vaporization = 2300KJ/Kg at 100°C.

Specific heat of liquids can be obtained using Kopp's rule from its chemical composition, i.e. C, H, N, S and O composition. As the data is not furnished due to unavailability of equipment so average values for C, H, N, S and O composition is taken from the literature as the properties of our bio-fuel lies considerably in the range of other similar products.

Thus,

C = 68; H = 8.7; N = 2.3; S = 0.085; O = 20.915

From Kopp's Rule, Specific Heat = 2.61 KJ/Kg K.

Now, distillation range for bio-fuel is,

Table 10: Distillation Range for Bio-Oil

Initial boiling Point (^oC)	90
10% Recovery (^oC)	98
30% Recovery (^oC)	250
50% Recovery (^oC)	312
70% Recovery (^oC)	342
90% Recovery (^oC)	358
Final Boiling Point (^oC)	362

Now,

$$(Total\ Energy\ Recovered) = (Energy\ by\ Fuel\ Gas) + (Energy\ by\ Oily\ Water) + (Energy\ by\ Biofuel) \quad (9)$$

Energy by fuel gas = 2023.2*0.5*(400-40) = 3,65,796 KJ = 365.796 MJ

Energy by Oily water = 3466.8*0.5*(400-100) + 3466.8*2300 + 3466.8*4.186*(100-40)

= 5,20,020 + 79,73,640 + 8,70,721.5 = 93,64,381.5 KJ = 9364.38 MJ

Energy by Bio-Fuel = (2650.8*0.5*(400-358)) + (265.08*2.61*(358-342)) + (2385.72*0.5*(358-342)) + (795.24*2.61*(342-312)) + (1855.56*0.5*(342-312)) + (1325.4*2.61*(312-250)) + (1325.4*0.5*(312-250)) + (1855.56*2.61*(250-98)) + (795.24*0.5*(250-98)) +(2385.72*2.61*(98-90)) + (265.08*0.5*(98-90)) + (2650.8*2.61*(90-40))

= 55666.8 + 11069.75 + 19085.76 + 62267.3 + 27833.4 + 214476.23 + 41087.4 + 736137.76 + 60438.24 + 49813.83 + 1060.32 + 345929.4

= 19,94,653.2 KJ = 1994 MJ

Total Energy Recovered = (365.8 + 9364.38 + 1994) MJ = 11724.18 MJ

Amount of cooling water@30°C required = 11724180/(4.186*40) = 70020 Kg = 70 tons

5.7. Equipment Size

5.7.1. Reactor

Cylindrical shape reactor made of carbon steel operating at 14.7 psi.

The reactor is assumed to work in a similar way to coke ovens used for coking of coal with a capacity of 12 tons processed at single run with a residence time of 20 hours.

Total Energy required for one run = 43,000 MJ = 40.76 M Btu

Time between two consecutive runs for discharging and loading = 1 hour

Total time for one run = 21 hours

Total no of runs per year = (365*24)/21 = 417 runs

Energy required per hour, Q = (40.76)/20 = 2.038 M Btu/hr

5.7.2. Crusher

Total raw material to be crushed per year = 417*12 = 5004 tons

Required crusher capacity = 5004/(365*24) = 0.571 tons/hr.

A crusher of capacity 1 ton/hr is used and operated at 0.571 tons/hr.

5.7.3. Condenser

1-4 Shell and tube exchanger with 21.25 inch shell inner diameter with a baffle spacing of 5 inch and 158 no of 16 inch long 13 BWG tubes with an outer diameter of 1 inch and a square pitch of 1.25 inch. Combineddirt factor of 0.003 should be provided.

Flow rate of vapors = (8140.8)/21 = 387.66 Kg/hr

Flow rate of cooling water = 70000/21 = 3333.33 Kg/hr

Inlet temperature of vapors = 400°C

Outlet temperature of vapors = 80°C

Inlet temperature of cooling water = 30°C

Outlet temperature of cooling water = 70°C

LMTD = 148.38°C R = 320/40 = 8 S = 40/(400-30) = 0.108 F_T = 0.88

Δt = 0.88*148.38 = 130.57°C

Shell Side (Cooling water):

Flow area = (21.25*0.25*5)/(144*1.25) = 0.1475 ft^2 = 137.03 cm^2 = 0.014 m^2

Mass Velocity =(3333.33)/(0.014) =2,38,095Kg/hrm^2 =66.1375Kg/m^2s = 5650080lb/hrft^2

Equivalent diameter = 0.99/12 = 0.0825 ft = 0.025 m

Viscosity of water = 0.547*10^{-3} N s/m^2

Thermal conductivity of water = 0.6 W/m K

Reynolds number = (0.025*66.1375)/(0.547*10^{-3}) = 3022.74

j_H = 29

h_o = 29*(0.6/0.025)*((4186*0.547*10^{-3})/0.6)$^{(1/3)}$ = 1087.65 W/m^2 K

Tube Side (Hot fluid):

Flow area = (158*0.515)/(144*4) = 0.141 ft^2 = 0.0131 m^2

Mass velocity = 387.66/(0.0131) = 29592.37 Kg/hr m^2 = 8.22 Kg/m^2 s = 702237.6lb/hrft^2

Viscosity of hydrocarbon vapor @240°C = 1.9*10^{-5} Kg/m s

Thermal conductivity of hydrocarbon vapor = 0.1385 W/m K

Reynolds number = (0.021*8.22)/(1.9*10^{-5}) = 9085.26

L/D = 16/0.0675 = 237

j_H = 35

h_i = 35*(0.1385/0.021)*((500*1.9*10^{-5})/(0.1385))$^{(1/3)}$ = 94.5 W/m^2 K

h_{io} = 94.5*0.81 = 76.545 W/m^2 K

Clean overall coefficient, U_C = (76.545*1087.65)/(76.545+1087.65) = 71.53 W/m^2 K

Overall design coefficient:

Total Surface Area = 158*16*0.2618 = 662 ft^2 = 61.5 m^2

U_D = ((11724.18*10^6)/(21*3600))/(61.5*130.57) = 55.02 W/m^2 K

Dirt Factor = (U_C - U_D)/(U_C*U_D) = (71.53-55.02)/(71.53*55.02) = 0.0042 m^2 K/W

5.7.4. Decanter

Input flow rate = 291.31 Kg/hr

Residence time = 18 Hrs

Volume of tank = 18*291.31 =5243.58Kg liquid product = (2272.04/1021.9) + (2971.54/1050)

= 2.223 + 2.83 = 5.053 m^3 = 1334.86 gal

Volume of tank taken = 1300 gallons

5.8. Cost Analysis

Cost analysis provides a rough estimate of the total investment required to setup a plant of particular capacity, operating cost of the plant and production cost of the product. Cost analysis data will enable us to determine whether setting up such a plant is economically feasible and beneficial to society or not.

Total investment consists of two parts:

- Fixed Capital: - Total cost of plant ready for start-up.
- Working Capital: - Additional investment needed, over and above the fixed capital, to start the plant and operate it to the point when income is earned.

5.8.1. Factorial Method to Determine Total Investment:

$$C_f = f_l * C_e \quad (11)$$

Where,

C_f = Fixed Capital Cost

f_l = Lang Factor depending on type of process

C_e = Total delivered cost of all major equipment.

Basic Procedure:

- Prepare material & energy balance, preliminary flow sheets, size major equipment and select material of construction.
- Estimate purchase cost of major equipment using literatures.
- Calculate Fixed Capital using Table 10.
- Working Capital = 10-20% of Fixed Capital.
- Total Investment = Fixed Capital + Working Capital.

Table 11: Lang Factors for Estimation of Fixed Capital[35]

		Process Type		
Sl. No.	**Item**	**Fluids**	**Fluids-Solids**	**Solids**
1	Major Equipment Purchase Cost (PCE)	1	1	1
f1	Equipment Erection	0.4	0.45	0.5
f2	Piping	0.7	0.45	0.2
f3	Instrumentation	0.2	0.15	0.1
f4	Electrical	0.1	0.1	0.1
f5	Buildings, Process	0.15	0.1	0.05
f6	Utilities	0.5	0.45	0.25
f7	Storage	0.15	0.2	0.25
f8	Site Development	0.05	0.05	0.05
f9	Ancillary Buildings	0.15	0.2	0.3
	Total Physical Plant Cost (PPC) = PCE*	3.4	3.15	2.8
	Total Physical Plant Cost (PPC)	1	1	1
f10	Design & Engineering	0.3	0.25	0.2
f11	Contractor's Fee	0.05	0.05	0.05
f12	Contingency	0.1	0.1	0.1
	Fixed Capital = PPC*	1.45	1.4	1.35

5.8.1.1. Major Equipment Costs

Reactor

Cost of cylindrical reactor made of carbon steel operating at 14.7 psi with an energy intake capacity of 2.038 MBtu/hr = 45,718$ (1985 basis, PCI = 325).

Cost of reactor @2010 (PCI = 586) = (586/325)*45718 = 82,433$

Crusher

Cost of Crusher of capacity 1tons/hr @1985 = 22,600$; Cost of crusher @2010 = 40,748$

Condenser

A 1-4 fixed head shell and tube heat exchanger made of stainless steel with heating surface area of 662 sqft and operating at pressure range of 1000 psi is required.

Cost of exchanger @1985 = 43,515$; Cost of exchanger @2010 = 78,461$

Storage Tanks

Cost of Storage Tank 1 (acting as Decanter) of volume 1300 gallons @1985 = 29,431$

Cost of Storage Tank 1 @2010 = 53,066$

Cost of Storage Tank 2 of capacity 10,000 gallons for storing bio-fuel @1985 = 58,160$

Cost of Storage Tank 2 @2010 = 1,04,867$

Cost of Storage Tank 3 of capacity 15,000 gallons for storing bio-fuel @1985 = 62,522$

Cost of Storage Tank 3 @2010 = 1,12,732$

Thus major equipment purchase cost = reactor + crusher + condenser + 3 storage tanks

= 4,72,307$ = Rs. 2,11,43,856

5.8.1.2.Total Investment

Major Equipment Purchase Cost (PCE) = Rs 2,11,43,856

Total Physical Plant Cost (PPC) = 1.95*PCE= Rs 4,12,30,519

Fixed Cost = 1.35*PPC = Rs 5,56,61,201

Working Capital = 0.10*Fixed Cost = Rs 55,66,120

Total Investment = Fixed Capital + Working Capital = Rs 6,12,27,321

5.8.2. Operating Cost

It is the cost of producing the product and is needed to judge viability of project and to choose between alternate processes.

$$\text{Annual Production Cost} = A + B + C \text{ (From Table 7)} \quad (12)$$

$$\text{Production Cost (per Kg)} = \frac{Annual\ Production\ Cost}{Annual\ Production\ Rate} \quad (13)$$

Table 12: Operating Cost[35]

Sl. No.	Item	Typical Values
	Variable Costs	
1	Raw Materials	From Material Balance
2	Miscellaneous Materials	10% of item (5)
3	Utilities	From Flow Sheet
4	Shipping & Packaging	Usually Negligible
	Sub Total A =	1+2+3+4
	Fixed Costs	
5	Maintenance	5-10% of Fixed Capital
6	Operating Labors	From Manning Estimates
7	Laboratory Costs	20-23% of item (6)
8	Supervision	20% of item (6)
9	Plant Overheads	50% of item (6)
10	Capital Charges	10% of Fixed Capital
11	Insurance	1% of Fixed Capital
12	Local Taxes	2% of Fixed Capital
13	Royalties	1% of Fixed Capital
	Sub Total B =	5+6+7+8+9+10+11+12+13
	Direct Production Costs =	A+B
14	Sales Expense	
15	General Overheads	
16	R & D	C = 20-30% of Direct Production Cost

Raw Materials

Cost of Raw Materials = 417*12*14000 = Rs 7,00,56,000

Miscellaneous Materials

Cost of Miscellaneous Materials = 0.10*0.05*5,56,61,201= Rs 2,78,306

Utilities

Chilled Water @30°C = ((417*70*1)/100)*(586/444) = 3082$ = Rs 17,247

Electricity = {1.5*1.32*{(417*43000000) + (14400*24*365) – (11724180*417)}}/100

= (1.5*1.32*13168161)/100 = 260730$ = Rs 1,16,72,149

Cost of Utilities = Rs 1,16,89,396

Maintainance

Cost of Maintanance = 0.05*5,56,61,201= Rs 27,83,060

Operating Labours

Cost of Operating Labour = 20*5*500*365 = Rs 1,82,50,000

Laboratory Costs

Laboratory Costs = 0.2*1,82,50,000= Rs 36,50,000

Supervision

Supervision Cost = 0.2*1,82,50,000= Rs 36,50,000

Plant Overheads

Plant Overheads = 0.5*1,82,50,000= Rs 91,25,000

Capital Charges

Capital Charges = 0.1*5,56,61,201= Rs 55,66,120

Insurance

Insurance = 0.01*5,56,61,201= Rs 5,56,612

Local Taxes

Local Taxes = 0.02*5,56,61,201= Rs 11,13,224

Royalties

Royalties = 0.01*5,56,61,201= Rs 5,56,612

Direct Production Costs = Rs 12,72,74,330

Sales Expense + General Overheads + R & D = 0.2*12,72,74,330= Rs 2,54,54,866

Annual Production Cost = 12,72,74,330+ 2,54,54,866= Rs 15,27,29,196

Income from sales of Bio-Fuel = 417*2594*50 = Rs 5,40,84,900

Income from sales of Oily Water = 417*3302*40 = Rs 5,50,77,360

Income from sales of Fuel Gas = 417*2023.2*4.4767*1.32 = Rs 49,85,478

Income from sales of Charcoal = 417*3859.2*3*1.623 = Rs 78,35,616

Total Income from Sales = Rs 12,19,83,354

Net Loss = Rs 3,07,45,842

CONCLUSION

6. Conclusion

- Groundnut de-oiled cakes are available in plenty and can be a good source of biomass.
- Maximum yield of bio-oil is obtained by pyrolysis of groundnut de-oiled cake at 450°C.
- Groundnut de-oiled cake has high volatile matter content which is converted and collected as bio-oil.
- The bio-oil obtained shows comparable fuel properties and can be treated as moderate grade commercial fuels.
- In order to utilize it as commercial transportation fuel certain enhancement in properties like density, viscosity, corrosiveness and volatility have to be taken care off.
- The bio-oil contains nearly 70 chemical compounds of varying carbon chain length from C_4-C_{27} and functional groups such as alkanes, alkenes, alkynes, alcohols, ketones, aldehydes, aromatics rings, amides, nitriles and nitro compounds.
- Charcoal obtained has a good calorific value, thus can be used as fuel but it can't be used as adsorbent as its surface area was quite low.
- Activation energy of the pyrolysis of groundnut de-oiled cake was found out to be in lower range thus enabling it to be used as a blend for easy pyrolysis of materials with higher activation energy.
- Industrial scale-up and economic assessment was performed for the process but a lot of assumptions had to be taken to simplify the calculations and to take care of the insufficient data. The result of the economic assessment was not satisfactory as it incurred a loss of 30 Million INR annually.
- In order to have proper economic assessment the following things are required to be taken care off: (a) compositional analysis of mixture of hydrocarbon vapors coming out of reactor

before getting condensed; (b) properties like specific heat, thermal conductivity, kinematic viscosity, latent heat of vaporization, etc. of every of component present in the hydrocarbon mixture are to be determined; (c) compositional analysis and physical property determination of oily water is also needed; (d) specific heat of bio-oil is also required.

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